

**Heterogeneous Chemistry of HONO on Liquid Sulfuric Acid:
A New Mechanism of Chlorine Activation on Stratospheric Sulfate Aerosols**

Renyi Zhang, Ming-Taun Leu*, and Leon F. Keyser

Earth and Space Sciences Division

Jet Propulsion Laboratory

California Institute of Technology, Pasadena, California 91109

(Submitted to *J. Phys. Chem.*, July 17, 1995)

* To whom correspondence should be addressed.

Introduction

Surface-catalyzed reactions occurring on sulfate aerosols enhance ozone destruction by reactive chlorine radicals (Cl and ClO) in the stratosphere.^{1,2} Heterogeneous reactions involving ClONO₂, HCl, and H₂O, for example, transform the inactive chlorine reservoir species (i.e. ClONO₂ and HCl) into forms (HOCl and Cl₂) that are easily photolyzed to produce atomic chlorine;³⁻⁵ ozone destruction then occurs in catalytic cycles initiated by Cl, via the ClO dimer mechanism^{6,7} or the reaction between ClO and BrO.⁸ Hydrolysis of N₂O₅ on sulfate aerosols also contributes to the global ozone destruction by deactivating odd nitrogen species (NO_x) during elevated sulfuric acid loading events.⁹⁻¹¹ In particular, this reaction has been proposed to mitigate the environmental impact of the projected fleet of High-Speed Civil Transport (HSCT) by converting the nitrogen oxide effluent into stable HNO₃.¹²⁻¹⁴

Both homogeneous and heterogeneous chemistry of HONO could have important implications in atmospheric chemistry. In the troposphere, nitrous acid is recognized as a key species in both indoor and outdoor air pollution. The gas phase chemistry of HONO plays an important role in the formation of hydroxyl radicals (OH), since HONO photolyses much rapidly to produce OH compared to ozone and formaldehyde photolysis. Because of its rapid photolysis at daytime, elevated concentrations of HONO have normally been observed only at night ranging up to a few ppbt at polluted sites, but recent observations reveal that non-zero daytime steady state HONO concentrations of 100-500 pptv have been observed in the clean troposphere.¹⁵ Despite its potential importance in atmospheric chemistry, the formation mechanism of HONO is not well established.¹⁶ Homogeneous gas phase reactions involving HO_x and NO_x are apparently too slow to account for the observed high levels of HONO. It is generally believed that heterogeneous processes are largely responsible for the HONO generation, among which are suggestions of HONO formation due to NO₂ hydrolysis on aqueous droplets¹⁷ and reduction of HNO₃ by SO₂ and by bromine ions (Br⁻) in acidic particles.¹⁸

HONO is produced by aircraft emissions due to aircraft engine combustion. Arnold et al.¹⁹ reported in situ measurements of trace species inside a DC-9 contrail around 10 km: the measured HONO concentrations inside the DC-9 plume were ~ 5 × 10⁹ molecules cm⁻³, about two orders of magnitude higher than the background values. In addition, sulfuric acid aerosols

nucleate homogeneously inside aircraft plumes due to SO_2 emissions.²⁰ *In situ* aerosol measurements of Concorde supersonic aircraft plumes confirm the existence of high aerosol densities inside aircraft plumes, with particles most likely consisting of 70-80 wt % H_2SO_4 .²¹ Hence, heterogeneous processes involving HONO on sulfuric acid particles may influence the plume chemistry, particularly in terms of hydrogen oxides HO_x .

Recent stratospheric measurements also suggest that photolysis of HONO could explain the observed anomalous OH and HO_2 concentrations shortly after sunrise,^{14,22} although the exact formation mechanism of HONO is still questionable. We have recently reported laboratory studies of heterogeneous interaction of peroxyntic acid (HO_2NO_2) with sulfuric acid and excluded the possibility that HONO is formed by heterogeneous decomposition of PNA on aerosols.²³

Burley and Johnston postulated that stratospheric sulfate aerosols may contain nitrosyl sulfuric acid ($\text{NO}^+\text{HSO}_4^-$).²⁴ They suggested that the heterogeneous reaction between HCl and $\text{NO}^+\text{HSO}_4^-$ may proceed on sulfuric acid particles, releasing gaseous nitrosyl chloride (ClNO). This process potentially provides a mechanism for chlorine activation in the stratosphere.

At present, assessments of the role of nitrous acid in atmospheric heterogeneous chemistry are limited by the lack of quantitative kinetic information. In this paper we investigate the interaction of gas-phase nitrous acid with liquid sulfuric acid and subsequent reaction with HCl to form nitrosyl chloride. We present laboratory measurements of the HONO uptake coefficient and the reaction probability of HCl with HONO on sulfuric acid. Analysis of the laboratory data reveals that, at elevated sulfuric acid loadings such as that after the eruption of Mt. Pinatubo, this process could result in an altered chlorine budget and an increased abundance of active chlorine. Furthermore, our results imply that heterogeneous processes involving HONO on sulfate aerosols play a key role in regulating the plume chemistry and can perturb the ozone balance,

Experimental

Measurements of heterogeneous reactions were performed using a fast flow-reactor in conjunction with chemical ionization mass spectrometer (CIMS) detection. The general experimental apparatus and procedures used here have been described previously,^{23,25-27} and only a brief description is given along with details specific to this work.

A horizontally-mounted flow reactor of inner diameter 2.8 cm was doubly jacketed and temperature regulated. Liquid sulfuric acid films were prepared by totally covering the inside wall of the flow reactor with acid solutions. The thickness of the liquid film was estimated to be about 0.1 mm. Temperature and water partial pressure in the flow reactor were adjusted to form acid compositions representative of stratospheric sulfate aerosols. For most experiments reported here, the water partial pressure was maintained closely at $\sim 5 \times 10^4$ Torr. As the temperature was varied from 207 K to 230 K, the acid composition changed from 60 to 75 wt %, estimated from the vapor pressures of the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ binary system.^{28,29} Typical experimental conditions were total pressure of 0.4 Torr and carrier gas flow velocity of 1700 to 2000 cm s^{-1} .

The uptake coefficient was determined from the decay corresponding to the reactant loss, using the standard cylindrical flow tube analysis. To account for the reactant radial and axial gradient in the flow reactor which arose when there was a large reactant wall loss, the observed first-order rate coefficient was corrected for gas-phase diffusion restrictions according to the method suggested by Brown.³⁰ The diffusion coefficients of HONO and HCl in helium were estimated to be 300 and 350 $\text{Torr cm}^2 \text{s}^{-1}$ at 220 K, respectively, both with a temperature dependence of $T^{1.75}$.³¹ The systematic error in the present measurements was estimated to be ± 15 %, including uncertainties in temperature, pressure, flow rate, and the correction associated with gas-phase diffusion.

HONO was synthesized by slowly adding -5 ml of 0.1 M NaNO_2 to ~ 10 ml of 40 wt % H_2SO_4 which was chilled (at 273 K) and vigorously stirred. The solution containing HONO was then transferred to a bubbler maintained at 273 K. Gaseous HONO was added to the flow tube along with a small He flow ($0.1 - 10.0 \text{ cm}^3 \text{ rein-l at STP}$) and further diluted in the main He flow (about $300 \text{ cm}^3 \text{ rein-l at STP}$) before contacting the liquid surface. An unjacketed movable injector was used to deliver HONO into the flow reactor. At low temperatures (< 230 K), H_2O (which was also eluded from the HONO source) condensed inside the cold injector and, thus, did not change the composition of the liquid film,

Gas-phase concentrations of the reactants and products were simultaneously monitored by the CIMS. Figure 1 shows a mass spectrum of SF_6^- reaction with the effluent from the HONO bubbler, HONO was detected in the CIMS as $\text{F}^\bullet \text{HONO}$ ($m/e = 66$), produced by a fluoride ion transfer with SF_6^- ,



We are not aware of any measurements of the rate coefficient for reaction 1. The HONO concentration in the neutral flow reactor was estimated by assuming the same rate coefficient as that for HNO_3 reaction with SF_6^- and by comparing the relative signal intensities between the two species under identical conditions.²³ HCl and ClNO were detected using SF_6^- corresponding to $\text{F}^\bullet + \text{HCl}$ ($m/e = 55$) and Cl^- ($m/e = 35$), respectively.³² A likely complication in the detection of ClNO came from the presence of some fluoride ion (F^- , $m/e = 19$), possibly formed by SF_6^- fragmentation (Figure 1), since the reaction between HCl and F^- also yielded Cl^- . These F^- concentrations, however, were too low to result in any appreciable amount of Cl^- and thus did not interfere with the ClNO detection. As shown in Figure 1, the HONO sample contained impurity as nitrogen dioxide NO_2 (NO_2^- , $m/e = 46$), but no HNO_3 (HNO_3 can be detected as $\text{F}^\bullet + \text{HNO}_3$ using SF_6^-). Nitrogen oxide NO could also be present in the HONO sample, but was undetectable in the CIMS due to its small electron affinity. Partial pressures of the reactants (HONO and HCl) were maintained at $(3\text{--}5) \times 10^{-7}$ Torr. The low reactant concentrations were essential to minimize the occurrence of secondary reactions of the product ions.

Results

HONO Uptake on Sulfuric Acid

Figure 2 displays the temporal evolution of the HONO signal as it was exposed to a sulfuric acid film at three different temperatures. The water partial pressure used in these experiments was about 5×10^{-4} Torr. The resultant sulfuric acid contents were 72, 65, and 61 wt % at temperatures of 224.6, 213.5, and 209.0 K, respectively. In 61 wt % sulfuric acid (Figure 2c), the gas-phase concentration of HONO dropped instantly upon exposure to H_2SO_4 at 0.5 rein, due to HONO adsorption into the liquid; the signal later returned to its original value as the film was saturated. Terminating the exposure at 2 min resulted in an opposite peak due to resorption. In contrast, loss of HONO in 72 wt % sulfuric acid (Figure 2a) was more pronounced and time-independent, characteristic of irreversible reactions occurring in the aqueous phase. No saturation

occurred for even longer durations ($t > 1$ hr), nor was any gas-phase product detected by the **CIMS**. For the intermediate sulfuric acid content (65 wt %, Figure 2b), some saturation was evident in the adsorption curve, but the HONO signal was never completely recovered.

Figure 3 shows the loss of HONO as a function of injector position as it was exposed to three sulfuric acid solutions: 73 wt % at 226 K (open triangles), 70 wt % at 220 K (filled circles), and 65 wt % at 213 K (open squares). It is seen in Figure 3 that the HONO signal decreased exponentially as a function of reaction distance in accord with first order kinetics. The slope of the decay curve was employed to derive the first-order rate coefficient; these coefficients lead to uptake coefficients of 0.10, 0.051, and 0.016, corresponding to the acid contents of 73, 70, 65 wt %, respectively.

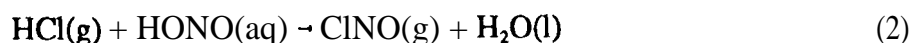
In Figure 4 are plotted uptake coefficients of HONO in sulfuric acid against the temperature. In these experiments, HONO uptake was studied by maintaining a constant water partial pressure of about 5×10^{-4} Torr and by varying temperature and allowing water vapor to equilibrate with the liquid. The top axis labels the estimated sulfuric acid content. Each point in the figure represents an average of more than three measurements, with the vertical bars indicating one standard deviation. The solid line is a linear least squares fit of the data, which results in an expression of $y = -0.9123 + 0.00435xT$ for the temperature range of 213-226 K. Figure 4 shows that the uptake coefficient decreases with decreasing acid content: y approaches 0.1 for about 73 wt % H_2SO_4 , whereas its value decreases by almost a factor of 5 for 65 wt % H_2SO_4 . This decline in y occurs primarily because of the adsorption/saturation processes, i.e. in dilute sulfuric acid the uptake is limited by volatility of HONO. For these experiments, it was necessary to keep the exposure time of HONO to the liquid film as short as possible, in order to minimize the saturation effect and obtain reproducible loss rate coefficient. Results of the uptake coefficients of HONO in sulfuric acid are summarized in Table 1.

Reaction of HCl with HONO

We studied the reaction probability between HONO and HCl on liquid sulfuric acid. The experiments were performed by first exposing the liquid film to HONO (typically within a few minutes) and then measuring the HCl uptake. Because HCl also physically dissolves in sulfuric

acid, it is essential to differentiate the reactive uptake from the physical uptake, when calculating the first-order loss coefficient. In general, HCl uptake in sulfuric acid depends both on the temperature and acidity: for temperatures between 210 and 230 K and acid contents between 60 and 75 wt % the time scale for saturating an acid film with HCl vapor would typically be less than a few minutes.^{5,33} Thus, as long as sufficient time is allowed for the system to reach equilibrium, the reaction probability between HONO and HCl can be accurately determined on the basis of the HCl decay. HCl vapor was introduced into the flow reactor through an unjacketed injector.

Figure 5 shows that loss of HCl on 71 wt % H₂SO₄ is irreversible and time-independent, which notably differs from the HCl uptake in absence of HONO.^{5,33} The disappearance of HCl upon exposure to H₂SO₄ inversely correlated with the appearance of ClNO, demonstrating that ClNO was liberated into the gas phase via the reaction of HCl with HONO dissolved in sulfuric acid,



Calibration of the relative detection sensitivities for HCl and ClNO in the CIMS gave a ClNO yield of nearly unity due to HCl loss. Note that the ClNO signal was multiplied by a factor of ten because the rate coefficient for SF₆⁻ reaction with ClNO is about an order of magnitude smaller than that of SF₆⁻ reaction with HCl.³²

Figure 6 is a semilog plot of measured HCl signal versus injector position. In all the three cases, the decay of HCl followed the first-order rate law. The observed first-order coefficients for HCl gave reaction probabilities of 0.022, 0.016, and 0.017, corresponding to 71, 68, and 62 wt % H₂SO₄, respectively. Thus, the reaction probability between HONO and HCl on sulfuric acid did not change significantly over the composition range of 62-71 wt %.

In Figure 7, values of reaction probability calculated from experiments such as those displayed in Figure 6 are presented as function of temperature at $P_{\text{H}_2\text{O}} \approx 5 \times 10^{-4}$ Torr. The HCl vapor pressure was maintained at 3×10^{-7} Torr. Contrary to the uptake coefficient of HONO on sulfuric acid, which increases monotonically with the acid content (Figure 4), the reaction probability between HCl and HONO may attain a minimum at compositions around 65 wt %. A likely explanation is that HCl volatility increases at low temperatures and in dilute sulfuric acid^{5,33} and, thus, leads to an increase in γ at low temperatures. Alternatively, it is also plausible

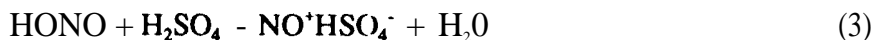
that the low values of y are due to scatter in the data. Results of y 's for reaction 2 are listed in Table 2.

Discussion

HONO Uptake on Sulfuric Acid

In general, HONO uptake in sulfuric acid exhibited two distinct features, dependent on the acidity: HONO uptake in more dilute sulfuric acid (< 61 wt %) appeared to comprise several steps, including adsorption, saturation, and resorption; loss of HONO in more concentrated solutions (> 72 wt %) was completely irreversible and time-independent. Transition between these two types of uptake occurred in the intermediate solutions (i.e. 61 to 72 wt %). These observed behaviors may be associated with the formation of nitrosyl sulfuric acid ($\text{NO}^+\text{HSO}_4^-$) and subsequent ionic reactions in the liquid, as proposed and documented at room temperature.

It has been previously realized that equilibrium of $\text{N}(+\text{III})$ species in highly acidic H_2SO_4 at room temperature may involve complex aqueous reactions between nitrogen species and sulfuric acid, Deschamps reported absorption spectra between 214 and 300 nm for 70-96 wt % H_2SO_4 containing 1 mole liter⁻¹ dissolved $\text{NO}^+\text{HSO}_4^-$; ³⁴ the spectrum showed only the nitrosonium ion (NO^+) in 96 wt % H_2SO_4 ; the amounts of H_2ONO^+ (hydrated nitrosonium ion) and NO^+ were equal in 88 wt % H_2SO_4 ; H_2ONO^+ dominated in 70.5 wt % H_2SO_4 , with a trace amount of HONO but no NO^+ . The proposed ionic mechanism is ^{24,34}



$\text{NO}^+\text{HSO}_4^-$ is an ionic species soluble in H_2SO_4 . In concentrated sulfuric acid, $\text{NO}^+\text{HSO}_4^-$ accumulates in the liquid and, upon reaching saturation, precipitates out as solid crystals to permit further accumulation.

Indeed, the process depicted in Figure 2c may not simply reflect the physical uptake (i.e. a reversible process), but rather a complex ionic reaction sequence (such as the one described

above) with HONO being the end product. $\text{NO}^+\text{HSO}_4^-$ is known to be unstable in excess water and reacts with H_2O to form the $\text{N}(+\text{III})$ species H_2ONO^+ and HONO. Our experiments with more dilute H_2SO_4 (less than 61 wt %) showed that HONO uptake was barely measurable, indicating very small solubility of HONO in sulfuric acid. The laboratory observations also showed that $\text{NO}^+\text{HSO}_4^-$ was stable in concentrated H_2SO_4 (> 72 wt %) and accumulated in the liquid (Figure 2c) at temperatures below ~ 230 K. We observed no precipitation of solid nitrosyl sulfuric acid crystals when continuously exposing HONO to H_2SO_4 over one hour, probably due to small HONO concentrations used in the experiments (typically about 5×10^{-7} Torr). Solubility of $\text{NO}^+\text{HSO}_4^-$ in sulfuric acid was estimated to be about a few percent by weight for stratospheric conditions.²⁴

In Fig. 3 the uptake coefficient (γ) of HONO increases as the temperature increases (at a fixed H_2O partial pressure) or as the acid content increases. This apparently reflects instability of $\text{NO}^+\text{HSO}_4^-$ in dilute sulfuric acid and subsequent re-generation and evaporation of HONO, consistent with the ionic mechanism noted above,

A first-order rate coefficient (k') for the reaction of HONO with H_2SO_4 can be determined from the measured uptake coefficient together with the estimated Henry's law volatility constant (H) and liquid-phase diffusion coefficient (D_l)^{35,36}

$$\gamma \approx \frac{4RTH\sqrt{k'D_l}}{\omega} \quad (7)$$

where R is the gas constant ($0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}$), T is the temperature, and ω is the thermal velocity of HONO. The liquid-phase diffusion coefficient for HONO in sulfuric acid was obtained from a cubic cell model:³⁷ for 70 wt % H_2SO_4 at 220 K, the value for D_l was $1.5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. The Henry's law constant for HONO in sulfuric acid was estimated to be $\sim 10^2 \text{ M atm}^{-1}$ for 70 wt % H_2SO_4 at 220 K.³⁸ Thus, we calculated a value $\sim 3 \times 10^6 \text{ s}^{-1}$ for k' for 70 wt % H_2SO_4 at 220 K using eq. 7. According to the theory of gas-particle reactions, the diffuse-reactive length ($l = \sqrt{D_l/k'}$), characteristic of the effective depth within the liquid over which the reaction occurs, was calculated to be $\sim 6 \times 10^4$ micrometer (μm).^{4,35} This estimate for l is small enough so that no limitation to the uptake of HONO is expected on small particles. In addition, it is worthwhile to point out that the Kelvin barrier, which arises from a pressure increase on a curved

surface, for **condensational** growth of small **particles**³⁹ plays no role in limiting the HONO uptake and reaction with **H₂SO₄**. Thus, the measured uptake coefficients should be applicable to the stratosphere.

Reaction of HCl with HONO

The reaction mechanism between HCl and HONO dissolved in sulfuric acid may also vary with the acid composition, depending on the **N(+ III)** species available in the liquid. Hence, it is likely that HCl reacts with the hydrated nitrosonium ion in dilute solutions



but with **nitrosyl** sulfuric acid in concentrated solutions



Also, at least for the case in concentrated **H₂SO₄** (> 70 wt %), the reaction between **HCl** and HONO dissolved in sulfuric acid occurs very near the gas-liquid interface, owing to exceedingly small **HCl solubility**. Using an estimated Henry's constant of $\sim 1 \text{ M atm}^{-1}$ for **HCl** in 70 wt % **H₂SO₄** at 220 K,^{5,33} the first-order rate **coefficient** due to HCl reaction with HONO is $\sim 2 \times 10^5 \text{ s}^{-1}$; this results in a value of $\sim 2 \times 10^{-3} \mu\text{m}$ for the diffuse-reactive length. Therefore, the correction needed to apply the results from bulk liquids to small aerosols is expected to be small.

Stratospheric Implications

Although detailed assessments of atmospheric implications for HONO heterogeneous reactions require simulations by full atmospheric models, we present here simple calculations to illustrate the major importance. For typical mid-latitude stratospheric conditions (i.e. temperatures between 220 and 230 K and sulfate aerosol compositions between 70-80 wt %), heterogeneous processing of the chlorine reservoir species **ClONO₂** and **HCl** are very **inefficient**.³⁻⁵ We calculate the production rate of **ClNO** due to the reaction of **HCl** with HONO on sulfate aerosols and compare this value with the well established gas phase conversion process between **hydroxyl** radical (OH) and **HCl** in the lower stratosphere ($\sim 100 \text{ mb}$ or 16 km). The loss rate of gaseous HONO onto sulfate aerosols is given by,

$$d[\text{HONO}]/dt = - \frac{1}{4} \gamma A \omega [\text{HONO}] \quad (10)$$

where A is the surface area density of sulfate aerosols and ω is the thermal velocity of HONO. The uptake coefficient of HONO in sulfuric acid is taken to be 0.07. The HONO concentration, $\sim 10^7$ molecules cm^{-3} , is based on measurements reported by Arnold et al. at around 10 km.¹⁹ (Note that this value is not constrained by stratospheric measurements. Additionally, the formation mechanism of atmospheric HONO is currently not well defined (ref 16).) We assume that the production rate of ClNO is approximately equal to the loss rate of HONO (i.e. $d[\text{HONO}]/dt \approx -d[\text{ClNO}]/dt$), since HCl (with concentrations of $\sim 2 \times 10^9$ molecules cm^{-3})⁴⁰ is far more abundant than HONO in the stratosphere (i.e. the rate-limiting step for reaction 2 is HONO incorporation into the aerosols). Using the aerosol surface densities of 6×10^{-9} $\text{cm}^2 \text{cm}^{-3}$ and 10^{-6} $\text{cm}^2 \text{cm}^{-3}$ for background aerosols and volcanic aerosols after the eruption of Mt. Pinatubo,⁴¹⁻⁴³ the ClNO production rates are 34 and 5600 molecules $\text{cm}^{-3} \text{s}^{-1}$, respectively. The value corresponding to the Mt. Pinatubo aerosol condition is more than ten times larger than the conversion rate between OH and HCl ($\sim 5 \times 10^{-4}$ molecules $\text{cm}^{-3} \text{s}^{-1}$).⁴ In the stratosphere, ClNO photodissociates rapidly, with a photolysis life time of ~ 560 s⁴⁰ and, hence, the reaction between HCl and HONO on sulfate aerosols could result in an increased abundance of reactive chlorine under elevated sulfuric acid loadings.

The fate of HONO emitted by the projected HSCT is governed by both photolysis and heterogeneous loss. Sulfuric acid particles nucleate homogeneously inside aircraft plumes due to SO_2 emissions.²⁰⁻²¹ Using a mean embryo radius of 0.4 nanometer (nm) and a particle number density of 10^9 cm^{-3} inside a newly formed aircraft plume,²⁰ the characteristic life-time of HONO due to loss on sulfate aerosols ($\tau = 4/(\gamma A \omega)$) would be about 90 seconds, considerably shorter than the photolysis life time of HONO (~ 820 s).⁴⁰ Thus, the heterogeneous process can lead to removal of a significant portion of gaseous HONO from aircraft effluent and largely regulate the plume chemistry (in terms of hydrogen oxides, HO_x). This is particularly true for nighttime emissions when HONO photolysis ceases. Our results demonstrate that sulfate aerosols can act as a temporary reservoir for HONO emitted by the HSCT and further interact with HCl, once available, to release ClNO. This process can affect the stratospheric ozone balance.

Conclusions

In this paper we have reported heterogeneous chemistry of HONO on liquid sulfuric acid. The uptake coefficient of HONO in sulfuric acid was found to increase with increasing acid content: γ approached 0.1 for about 73 wt % H_2SO_4 , whereas its value decreased by almost a factor of 5 for 65 wt % H_2SO_4 . The laboratory observations showed that HONO uptake on sulfuric acid consisted of the adsorption/saturation processes in dilute sulfuric acid, but was completely irreversible in concentrated sulfuric acid, consistent with the formation of nitrosyl sulfuric acid $\text{NO}^+\text{HSO}_4^-$ and the N(+III) species H_2ONO^+ in the liquid. The results also showed that $\text{NO}^+\text{HSO}_4^-$ was stable and accumulated in concentrated solutions (> 70 wt % H_2SO_4) at temperatures below 230 K, but was unstable and quickly re-generated HONO in dilute solutions (< 70 wt %). Heterogeneous reaction between HCl and HONO dissolved in sulfuric acid was also investigated. Gaseous nitrosyl chloride was identified to be the reaction product. Reaction probabilities between HCl and HONO ranged from 0.01 to 0.02 for 60-72 wt % H_2SO_4 . Analysis of the laboratory data reveals that the reaction of HCl with HONO on sulfate aerosols can provide a mechanism for chlorine activation and, subsequently, affect stratospheric ozone balance, during elevated sulfuric acid loadings after volcanic eruptions or due to emissions from the projected High-Speed Civil Transport (HSCT). Hence, the present results may have important implications on the environmental impact of aircraft emissions.

Acknowledgements

The research was performed at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration (NASA). We thank H.S. Johnston for helpful discussions and C.A. Brock and J.C. Wilson for providing information on aerosol measurements inside aircraft plumes.

REFERENCES AND NOTES

- (1) Solomon, S, *Nature* **1990**, 347, 347.
- (2) Anderson, J. G.; Toohey, D, W.; **Brune, W.H.** *Science* **1991**, 251, 39.
- (3) **Molina, M. J.; Zhang, R.**; Wooldridge, P. J.; McMahon, J. R.; Kim, J. E.; **Chang, H. Y.**; Beyer, **K.D.** *Science* **1993**, 261, 1418,
- (4) Hanson, D.R.; Ravishankara, A.R.; Solomon, S. *J. Geophys. Res.* **1994**, **99**, 3615.
- (5) **Zhang, R**; Leu, M.T.; Keyser, L.F. *J. Phys. Chem.* **1994**, **98**, 13563.
- (6) **Molina, L.T.**; **Molina, M.J.** *J. Phys. Chem.* **1987**, **91**,433.
- (7) **Sander, S.P.**; Friedl, R.R.; Yung, Y.L. *Science* **1989**,245, 1095.
- (8) McElroy, M. B.; Salawitch, R. J.; Wofsy, S, C.; Logan, J.A. *Nature* **1986**, **321**, 759.
- (9) Hofmann, D.J; Solomon, S. *J. Geophys. Res.* **1989**, **94**, 5029.
- (10) **Brasseur, G. P.**; **Granier, C.**; Walters, S. *Nature* **1990**, 348, 626.
- (11) Rodriguez, J. M.; Ko, M. K. W.; Sze, N.D. *Nature* **1991**, 352, 134.
- (12) **Pitari, G.**; **Rizi, V.**; **Ricciardulli, L.**; Visonti, G. *J. Geophys. Res.* **1993**, **98**, 23141.
- (13) Tie, X,X, et al. *J. Atmos. Chem.* **1994**, 18(2), 103.
- (14) **Wennberg, P.O.** et al. *Science*, **1994**, 266, 398.
- (15) Vecera, Z.; Dasgupa, P.K. *Environ, Sci. Technol.* **1991**, 25, 255.
- (16) **Calvert, J. G.**; Yarwood, G.; Dunker, A.M. *Res. Chem. Intermed.* **1994**, **20**, 463.
- (17) **Bambauer, A.**; Brantner, B.; **Paige, M.**; Novakov, T. *Atmos. Environ.* **1994**,28,3225 and references cited therein.
- (18) Li, S.M. *J. Geophys. Res.* **1994**, 99,469.
- (19) Arnold, F.; Scheid, J.; **Stilp, I%**; **Schlager, H.**; Reinhardt, M.E. *Geophys. Res. Lett.* **1992**, **19**, 2421.
- (20) **Karcher, B.**; **Peter, Th.**; Ottmann, R. *Geophys. Res. Lett.* **1995**, 22, 1501.
- (21) **Brock, C. A.**; Wilson, J. C., private communication, 1995.
- (22) **Salawitch, R.J.** et al. *Geophys. Res. Lett.* **1994**, **21**, 2551.
- (23) **Zhang, R**; **Leu, M.T.**; Keyser, L.F. *J. Phys. Chem.*, submitted, 1995,
- (24) Burley, J. D.; Johnston, H.S. *Geophys. Res. Lett.* **1992**, **19**, 1363,

- (25) Zhang, R.; Leu, M.T.; Keyser, L.F. *Geophys. Res. Lett.* **199S**, 21, 1493.
- (26) Zhang, R.; Leu, M.T.; Keyser, L.F. *J. Geophys. Res.*, in press.
- (27) Leu, M. T.; Timonen, R. S.; Keyser, L.F.; Yung, Y.L. *J. Phys. Chem.* in press,
- (28) Zeleznik, F.J. *J. Phys. Chem. Ref. Data* 1991, 20, 1157.
- (29) Zhang, R.; Wooldridge, P.J.; Abbatt, J.P.D.; Molina, M.J. *J. Phys. Chem.* 1993,97,7351.
- (30) Brown, R.L. *J. Res. Natl. Bur. Stand. (U. S.)* **1978**, 83, 1.
- (31) Marrero, T.R; Mason, E.A. *J. Phys. Chem. Ref. Data*, 1972, 1, 3.
- (32) Ikezoe, Y.; Matsuoka, S.; Takebo, M.; Viggiano, A. Gas *Phase Ion-Molecule Reaction Rate Constants through 1986*, Maruzen Company, Ltd.: Tokyo, 1987.
- (33) Hanson, D.R.; Ravishankara, A.R. *J. Phys. Chem.* 1993, 97, 12309.
- (34) Deschamps, J.M.R. *Compte rend.*, 1957, 245, 1432.
- (35) Schwartz, S.E. In *Chemistry of Multiphase Atmospheric Systems*; Jaeschke, W., Ed.; NATO ASI Series, Vol. G6; NATO: Brussels, 1986.
- (36) Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E.; Gardner, J. A.; Watson, L. R.; Van Doren, J. M.; Davidovits, P. *J. Phys. Chem.* 1989, 93, 1159.
- (37) Luo, B. P.; Clegg, S. L.; Peter, T.; Muller, R.; Crutzen, P.J. *Geophys. Res. left.* **1994**,21, 49.
- (38) Wagman, D.D. et al. *J. Phys. Chem. Ref. Data* 1982, 11,2.
- (39) Pruppacher, H.R.; Klett, J.D. *Microphysics of Clouds and Precipitation*, D. Reidel Publishing Co., Dordrecht: Holland, 1980.
- (40) DeMore, W. B.; Sander, S. P.; Howard, C.J.; Ravishankara, A. R.; Golden, D. M.; Kolb, C. E.; Harnpson, R. F.; Kurylo, M. J.; Molina, M.J. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*; JPL Publ. 94-26, NASA, 1994.
- (41) Turco, R.P.; Whitten, R. C.; Toon, O.B. *Rev. Geophys.* 1982, 20, 233.
- (42) Deshler, T.; Hofmann, D. J.; Johnson, B. J.; Rozier, W.R. *Geophys. Res. Left.* **1992**, 19, 199.
- (43) Wilson, J.C. et al. *Science* 1993, 261, 1140.

Table 1. Summary of the Uptake Coefficient of HONO in Sulfuric acid^a

Temperature (K)	H ₂ SO ₄ wt % ^b	$\gamma \pm 1\sigma$
213.5	65.3	0.016 ± 0.0009
216.4	67.4	0.040 ± 0.0078
218.5	68.7	0.033 ± 0.0012
218,6	68.8	$0,026 \pm 0.0154$
218.6	68.8	$0.037 * 0.0067$
220.4	69.9	$0.059 * 0.0119$
222.6	71.3	0.072 ± 0.0193
222,6	71.3	$0.060 * 0.0054$
224.6	72.3	0.048 ± 0.0085
224.7	72.4	$0.047 * 0.0054$
226,1	73.0	0.091 ± 0.0162

^a The experiments were performed by maintaining constant water partial pressure at 5×10^{-4} Torr and by regulating temperature between 213 and 226 K. Each point is an average of more than three measurements. Experimental conditions are $P_{\text{He}} = 0.4$ Torr, $V = 1700$ to 2000 cm s⁻¹, and $P_{\text{HONO}} \approx 5 \times 10^{-7}$ Torr.

^b Estimated from the temperature and water partial pressure.

Table 2. Summary of the Reaction Probability of HCl with HONO
Dissolved in Sulfuric acid^a

Temperature (K)	H ₂ SO ₄ wt % ^b	$\gamma \pm 1\sigma$
207.9	60.8	0.020 * 0.0049
209.1	61.7	0.018 * 0.0030
213.2	65.1	0.011 * 0.0040
217.3	68.0	0.016 * 0.0010
218.6	68.8	0.016 ± 0.0008
220.4	69.9	0.019 * 0.0014
222.6	71.3	0.020 * 0.0019

^a The experiments were performed by maintaining constant water partial pressure at 5×10^{-4} Torr and by regulating temperature between 208 and 223 K. Each point is an average of more than three measurements. Experimental conditions are $P_{\text{He}} = 0.4$ Torr, $V = 1700$ to $2000 \text{ cm}^3 \text{ s}^{-1}$, $P_{\text{HONO}} \approx 5 \times 10^{-7}$ Torr, and $P_{\text{HCl}} = 3 \times 10^{-7}$ Torr.

^b Estimated from the temperature and water partial pressure.

Figure Captions

- Figure 1. Mass spectrum of SF_6^- reaction with the effluent from a HONO bubbler. $\text{F}^\bullet\text{HONO}$ is formed by a fluoride ion transfer from SF_6^- to HONO. Impurity in the HONO sample is recognized mainly as NO_2 (NO_2^- , $m/e = 46$). Some fluoride ions are also detected in the CIMS, possibly formed by electron impact of SF_6 .
- Figure 2. Variation of HONO signal as it was exposed and not exposed to 5 cm-length of (a) 72 wt % H_2SO_4 at 224.6 K, (b) 65 wt % H_2SO_4 at 213.5 K, and (c) 61 wt % H_2SO_4 at 209.0 K. The injector was moved upstream at about 0.5 min and returned to its original position at 2 min. Experimental conditions: $P_{\text{HONO}} \approx 5 \times 10^7$ Torr, $P_{\text{He}} = 0.4$ Torr, $P_{\text{H}_2\text{O}} \approx 5 \times 10^{-4}$ Torr, and flow velocity = 1700 to 1900 cm s^{-1} .
- Figure 3. Plot of the HONO signal as a function of reaction distance on three acid solutions: 73 wt % H_2SO_4 at 226 K (open triangles), 70 wt % H_2SO_4 at 220 K (filled circles), and 65 wt % H_2SO_4 at 213 K (open squares). The lines are linear least squares fits through the data. Experimental conditions are similar to those in Figure 2.
- Figure 4. Uptake coefficient (γ) of HONO on liquid sulfuric acid as a function of temperature at $P_{\text{H}_2\text{O}} = 5.0 \times 10^4$ Torr. The estimated acid content (top axis) ranged from about 65 to 75 wt %, as the temperature was varied from 213 to 230 K. Each point in the figure is an average of more than three measurements. The error bars represent one standard deviation of each determination. The solid line is a linear least squares fit through the data. Experimental conditions are similar to those in Figure 2.
- Figure 5. Variation of the HCl signal when exposed to a 3.5 cm-length of HONO-doped sulfuric acid film at 222 K. The disappearance of HCl upon exposure to H_2SO_4 at ~ 0.7 min was accompanied by the appearance of ClNO . The exposure was terminated at ~ 2 min. The acid content of the film was estimated to be ~ 71 wt %. Experimental conditions: $P_{\text{HONO}} \approx 5 \times 10^{-7}$ Torr, $P_{\text{HCl}} = 3 \times 10^{-7}$ Torr, $P_{\text{He}} = 0.4$ Torr, $P_{\text{H}_2\text{O}} \approx 5 \times 10^{-4}$ Torr, and flow velocity = 1700 to 1900 cm s^{-1} .
- Figure 6. Plot of the HCl signal as a function of reaction distance on three HONO-doped

sulfuric acid solutions: 71 wt % at 223 K (open squares), 68 wt % at 217 K (filled circles), and 62 wt % at 209 K (open triangles). The lines are linear least squares fits through the data. Experimental conditions are similar to those in Figure 5.

Figure 7. Reaction probability γ (γ) of HCl with HONO dissolved in sulfuric acid, The reaction probability was obtained from the observed HCl decay rate, when HCl was exposed to HONO doped sulfuric acid. Each point in the Figure is an average of more than three measurements, The error bars represent one standard deviation of each determination. Experimental conditions are similar to those in Figure 5.

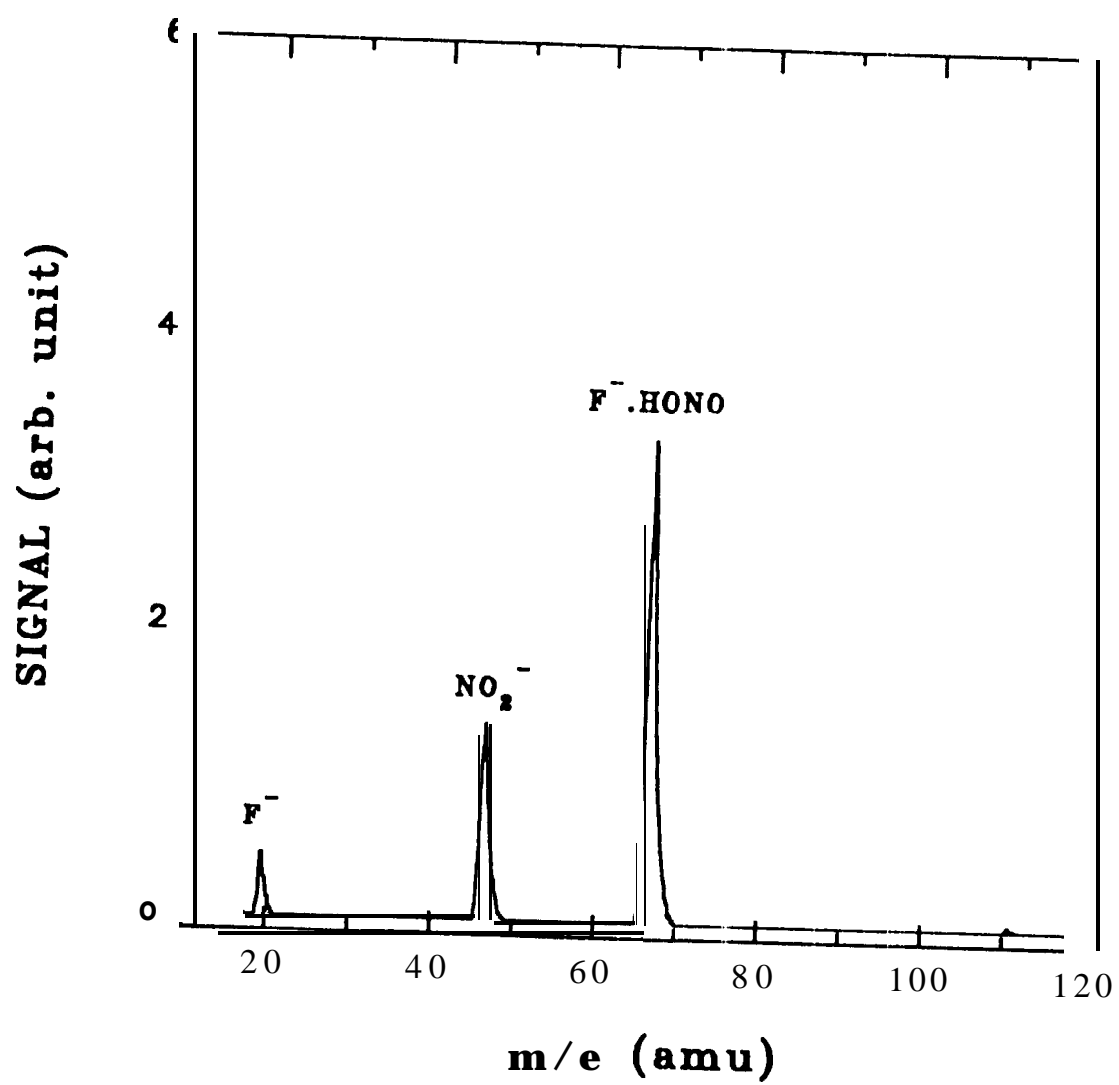


Fig. 1

SIGNAL (arb. units)

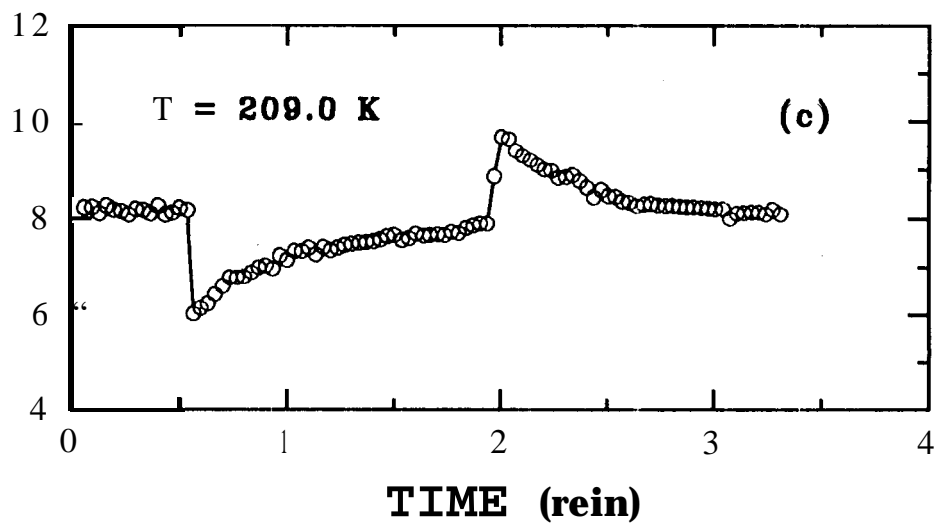
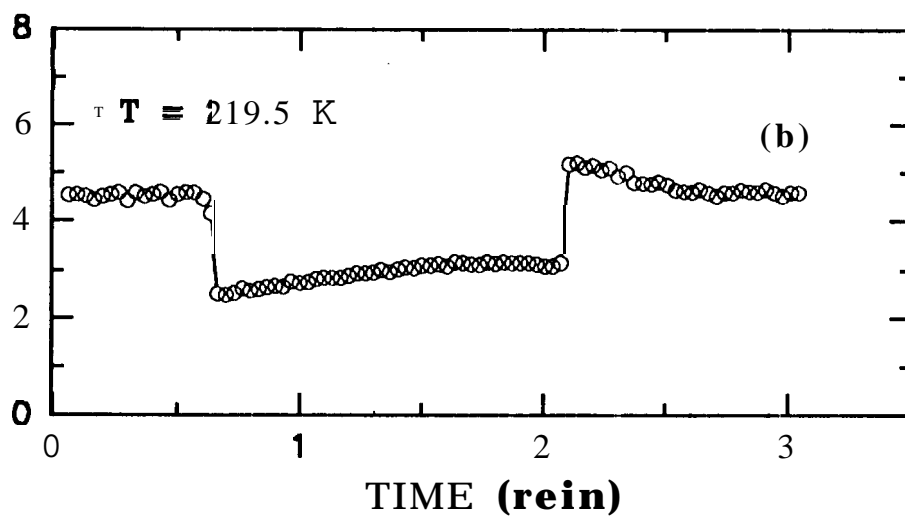
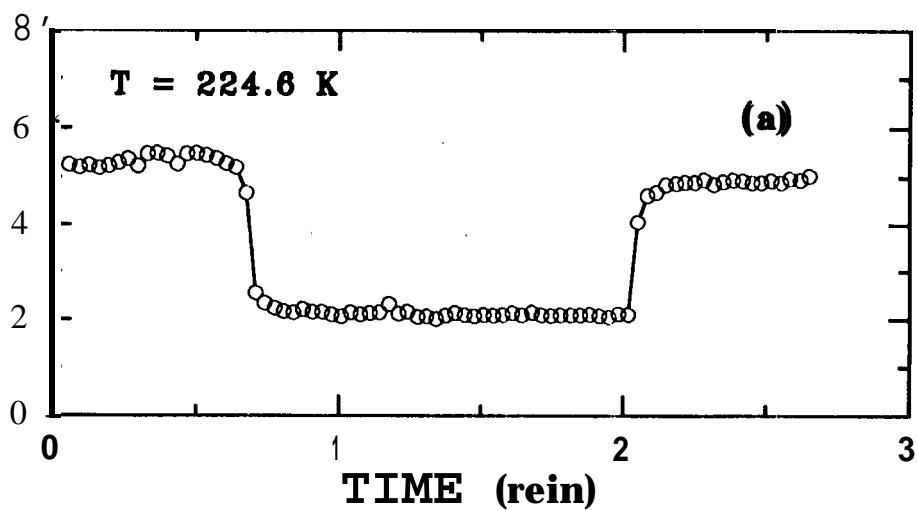


Fig. 2

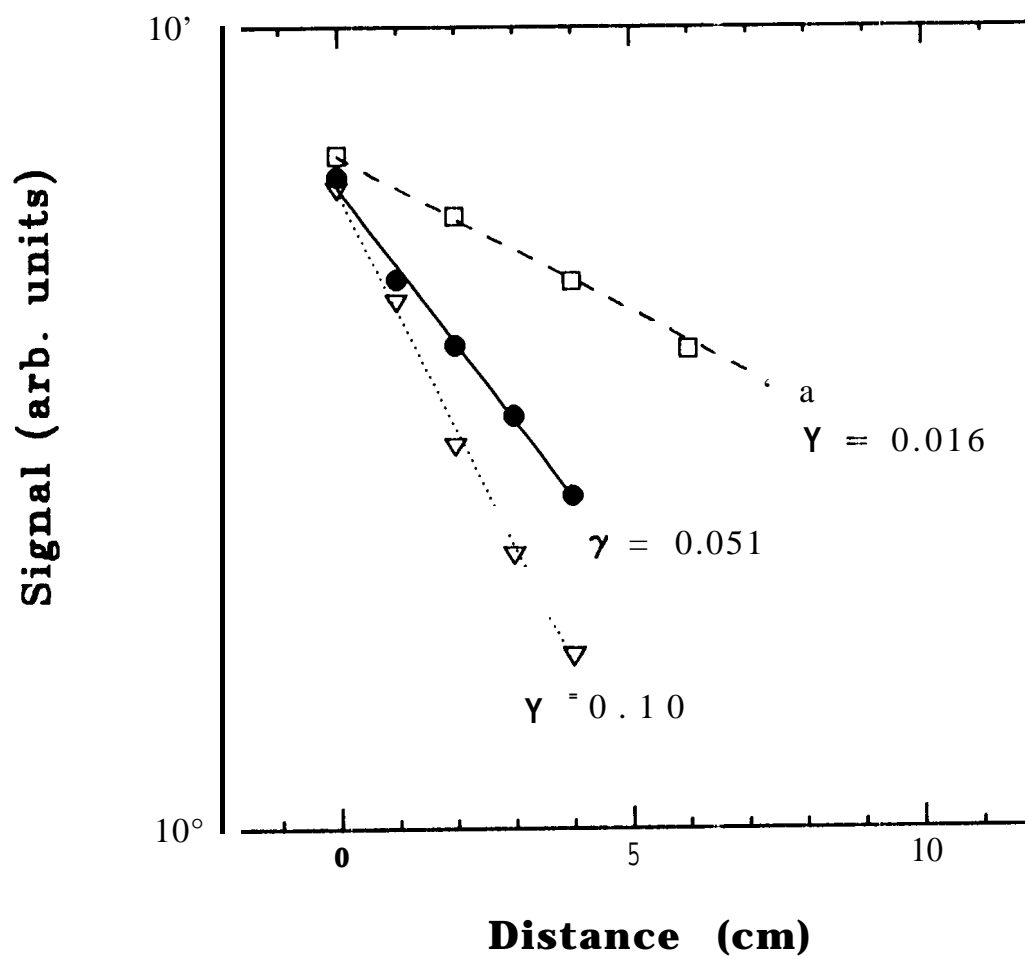


Fig. 3

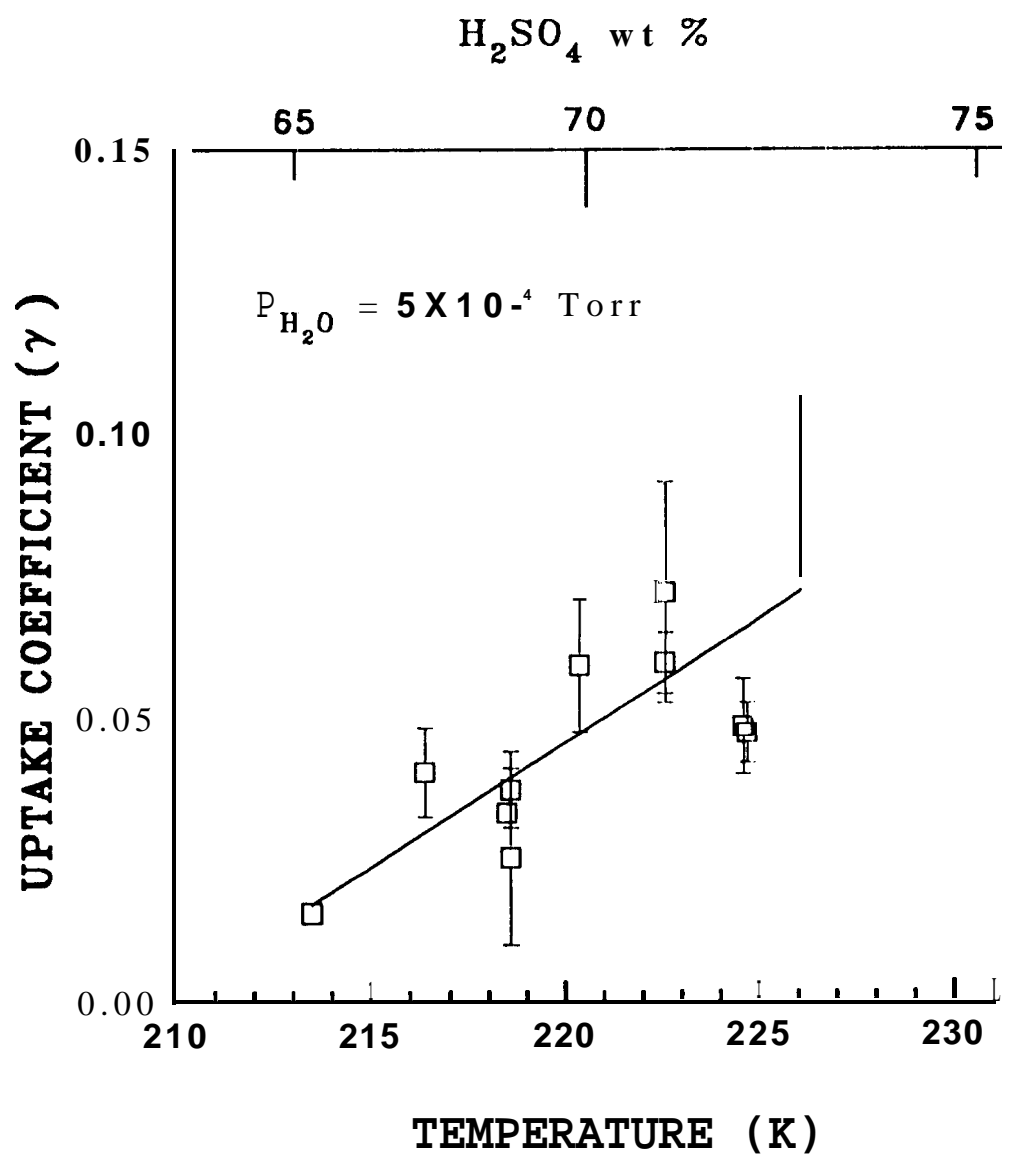


Fig 4

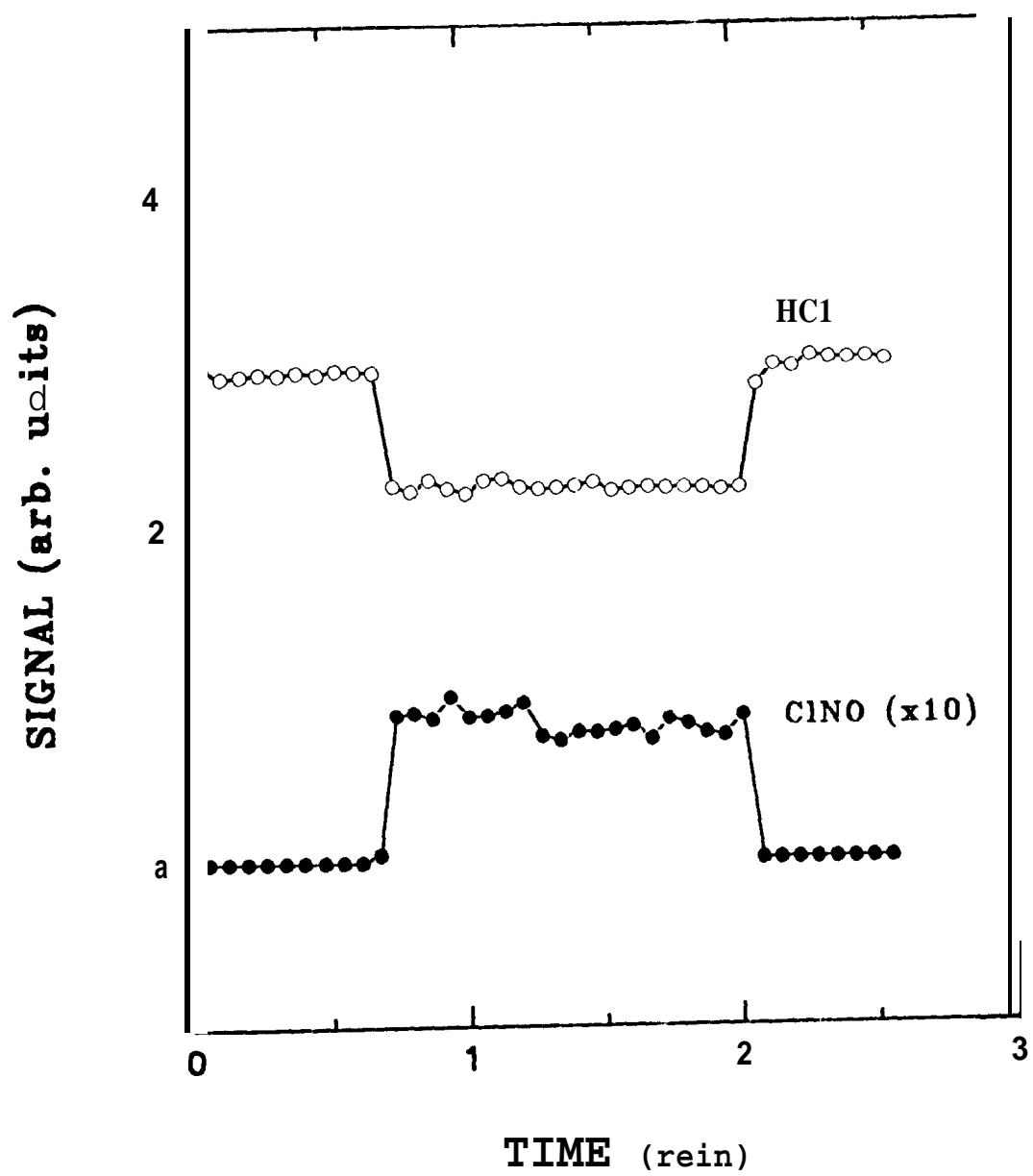


Fig. 5

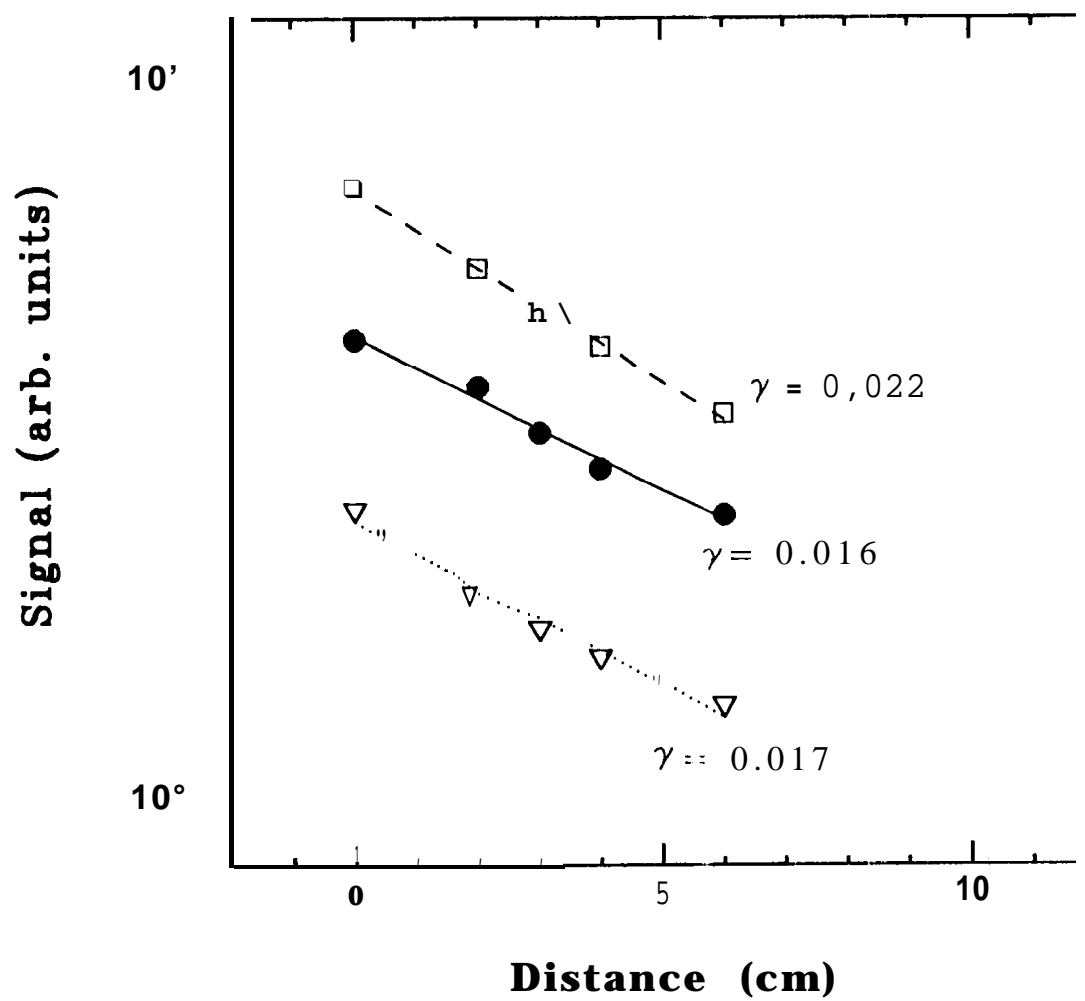


Fig. 6

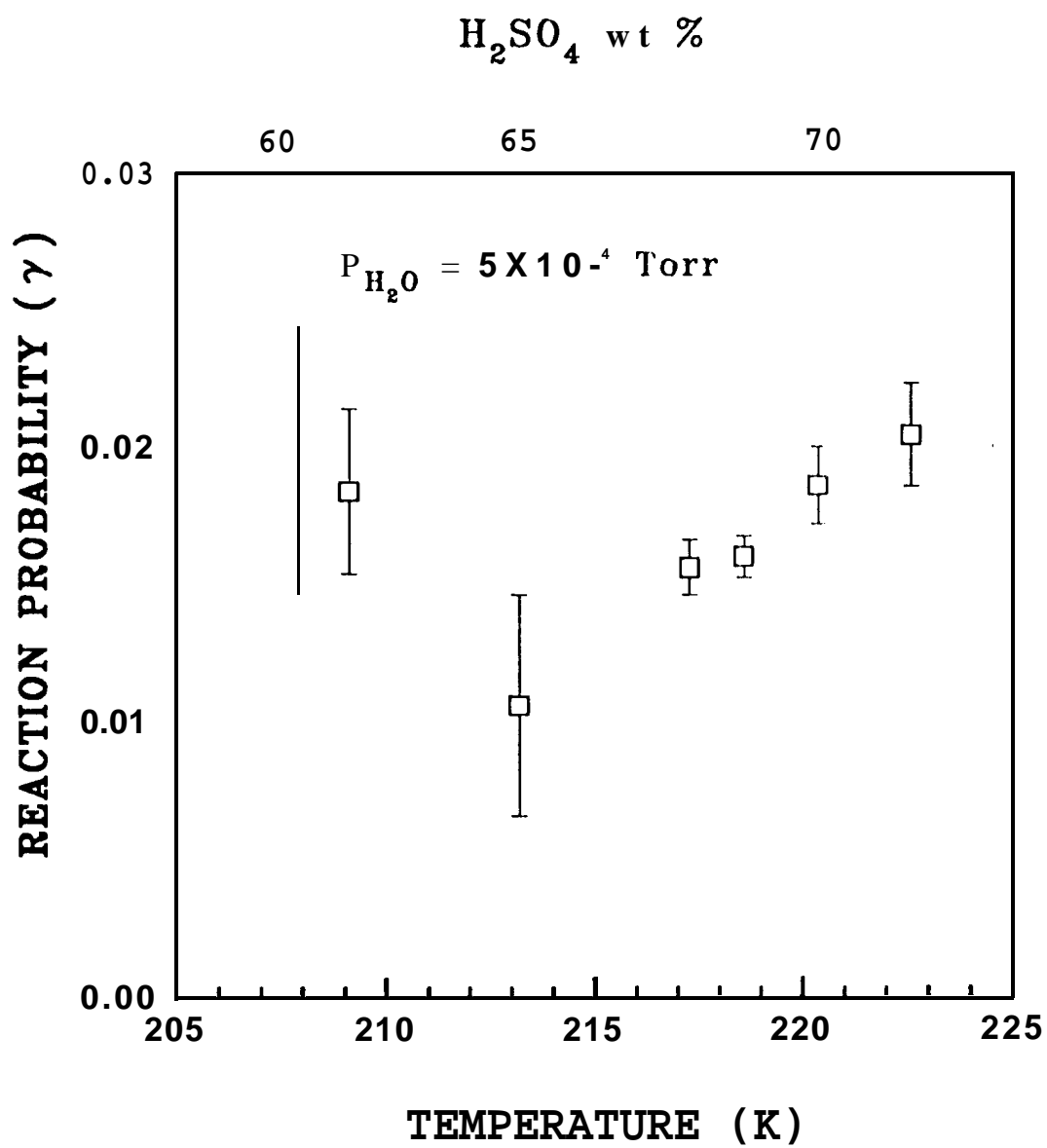


Fig. 7